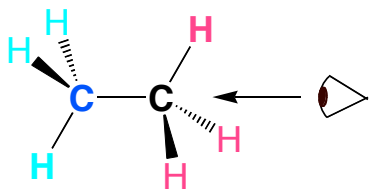
Chapter 4: Stereochemistry of Alkanes and Cycloalkanes

Stereochemistry: three-dimensional aspects of molecules

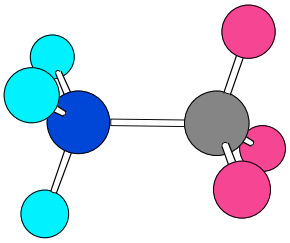
Conformation: different geometric arrangements of atoms that result from rotations about single (σ) bonds

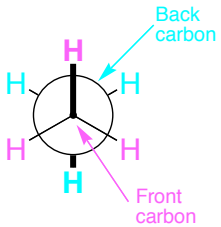
Conformer: a specific conformation of a molecule

Conformations of Ethane CH_3-CH_3

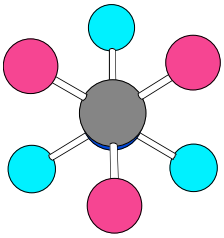


Sawhorse

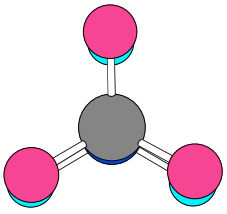




Newman projection



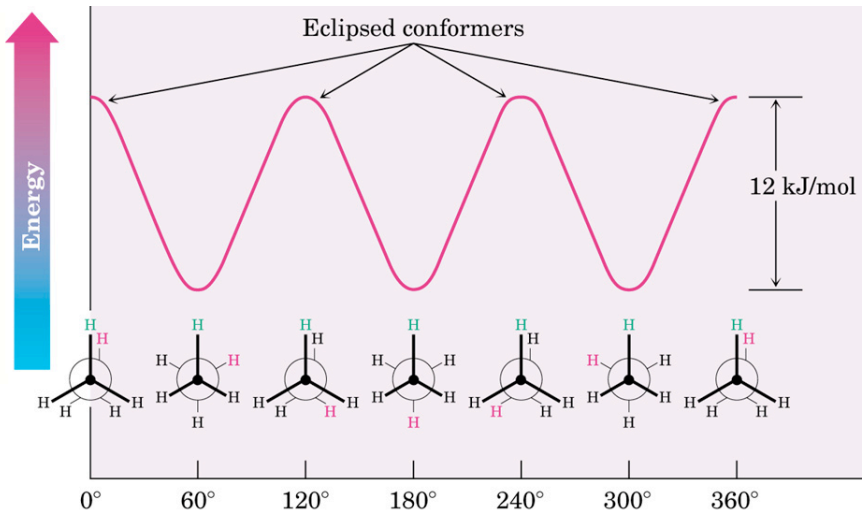
Staggered



Eclipsed

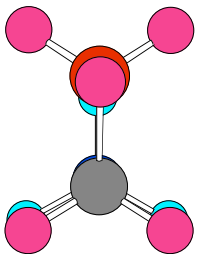
Energy vs. Dihedral Angle for Ethane

http://www2.chem.ucalgary.ca/Flash/ethane.html

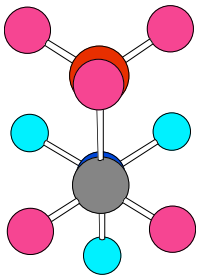


Torsional Strain: strain (increase in energy) due to eclipsing groups

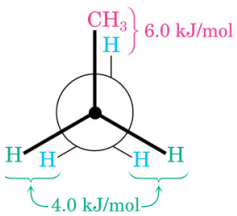
Conformations of Propane

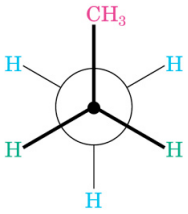


eclipsed



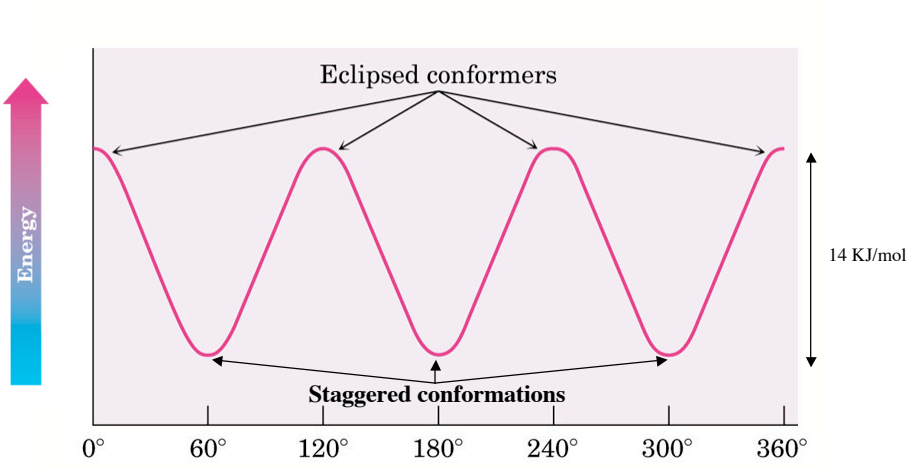
staggered



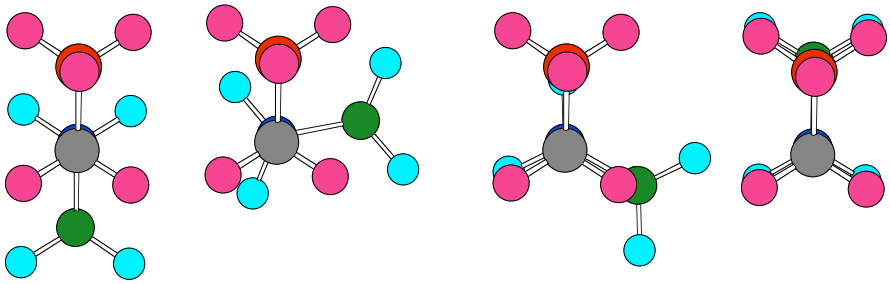


Staggered propane

Energy vs. Dihedral Angle for Propane

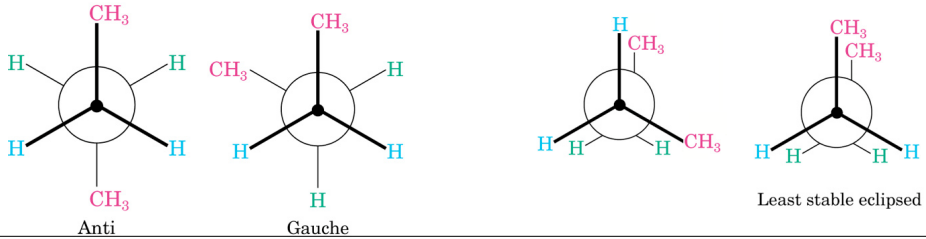


Conformations of Butane

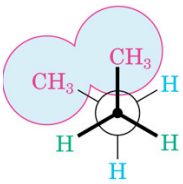


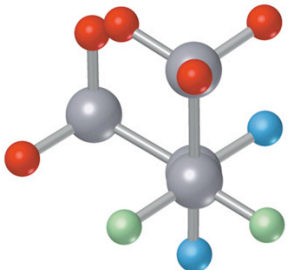
anti gauche CH_3 - H CH_3 - CH_3

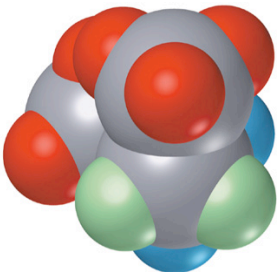
Staggered Eclipsed



Steric Strain: repulsive interaction that occurs when two groups are closer than their atomic radii allow

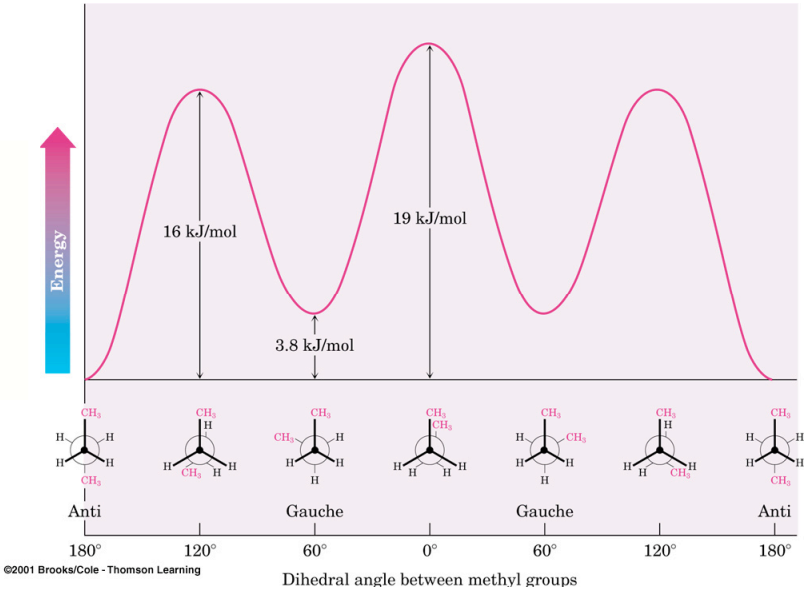






Energy vs Dihedral Angle for Butane

http://www2.chem.ucalgary.ca/Flash/butane.html



Strain Energy of Alkane Conformations

H - H eclipsed	4.0 KJ/mol	torsional strain
H - CH_3 eclipsed	6.0 KJ/mol	mostly torsional strain
CH_3 - CH_3 eclipsed	11 KJ/mol	torsional and steric strain
CH_3 - CH_3 gauche	3.8 KJ/mol	steric strain

Torsional Strain: strain (increase in energy) due to eclipsing groups
Steric Strain: repulsive interaction that occurs when two groups are closer than their atomic radii allow

Baeyer Strain Theory

Angle Strain: strain due to deforming a bond angle from its ideal value

Heats of Combustion of Cycloalkane:

the more strain a compound is, the more heat it released upon combustion

$$C_nH_{2n} + 3n/2\ O_2 \longrightarrow n\ CO_2 + n\ H_2O + \text{heat}$$

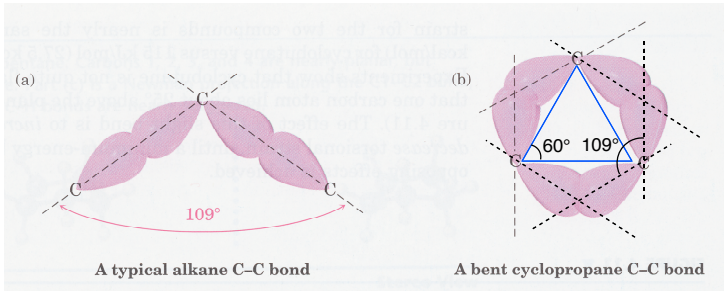
cycloalkane (can be measured)

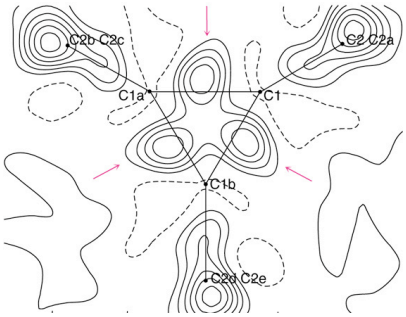
$$\text{Total Strain Energy} = \left(\left[\text{Sample } \Delta H_{comb} \text{ per } -CH_2- \right] - \left[\text{Reference } \Delta H_{comb} \text{ per } -CH_2- \right] \right) \bullet n$$

Figure 4.8 (page 122)

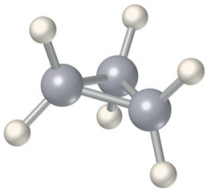
	Cycloalkane	Ring Size (n)	ΔH_{comb} KJ/mol	ΔH_{comb} per $-CH_2-$ KJ/mol	Total Strain Energy
Strain rings		3	2090	698	115
		4	2744	686	110
Common rings		5	3220	664	27
		6	3952	659	0
		7	4637	662	27
Medium rings		8	5310	664	42
	Cyclononane	9	5981	665	54
	Cyclodecane	10	6636	664	50
< 12 Large rings	Cyclopentadecane	15	9985	659	0
	Alkane reference			659	0

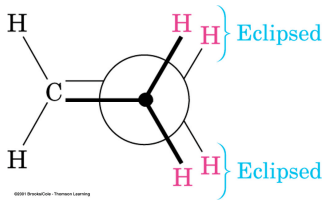
Bonding in Cyclopropane (section 4.7)





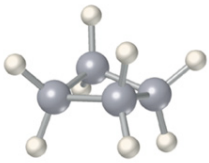
Cyclopropane: flat

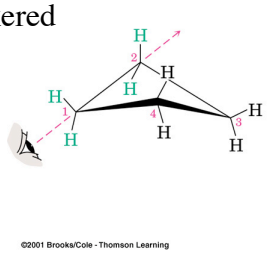


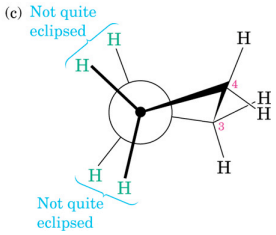


Total of 6 H-H eclipsing interactions

Cyclobutane: puckered







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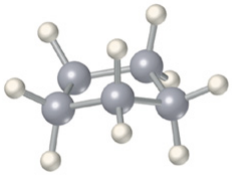
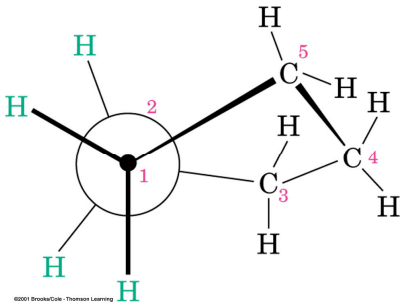
Puckering of cyclobutane increases angle strain but partially relieves torsional strain

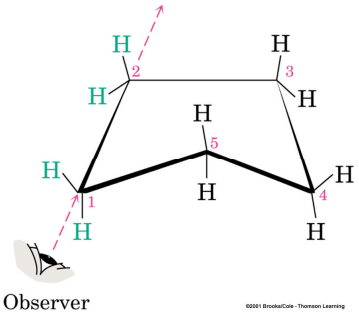
Cyclopentane



Strain free according to Baeyer
$\Delta H°_{comb}$ indicates some strain
Almost no angle strain
Some torsional strain

Cyclopentane puckers to relieve torsional Strain although this increases angle strain





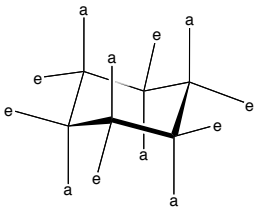
Envelope conformation

Cyclohexane: strain free, favored conformation is a chair

Chair cyclohexane has two types of hydrogens:

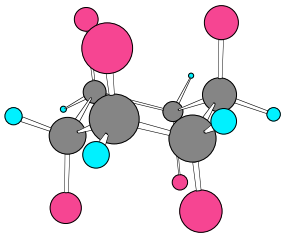
- axial: C-H axis is "perpendicular" to the "plane of the ring"
- equatorial: C-H axis is "parallel" to the "plane of the ring"

Chair cyclohexane has two faces; each face has alternating axial and equatorial -H's

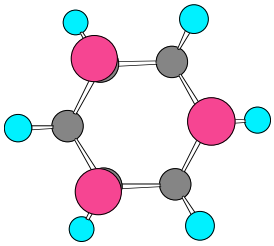


axial

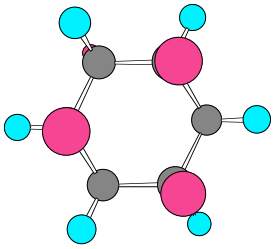
equatorial



Chair cyclohexane



top



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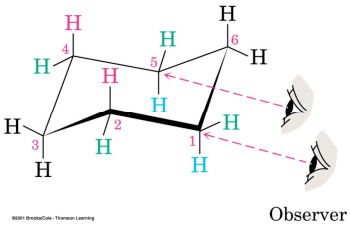
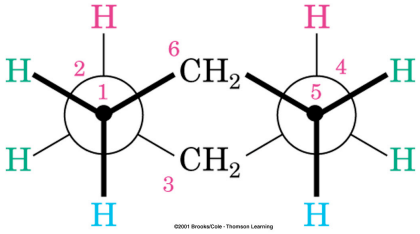


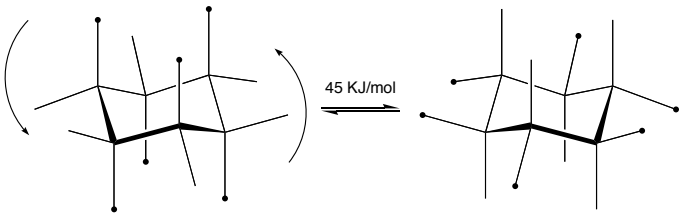


All -H/-H interactions are staggered

No torsional strain

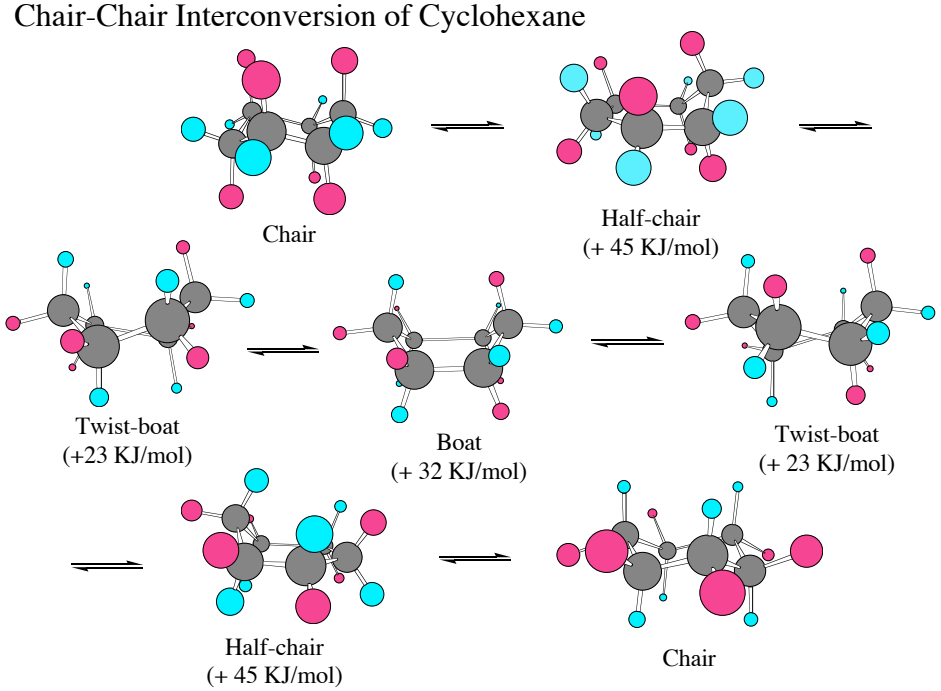
No angle strain

Chair-Chair Interconversion (ring flip): 45 KJ/mol



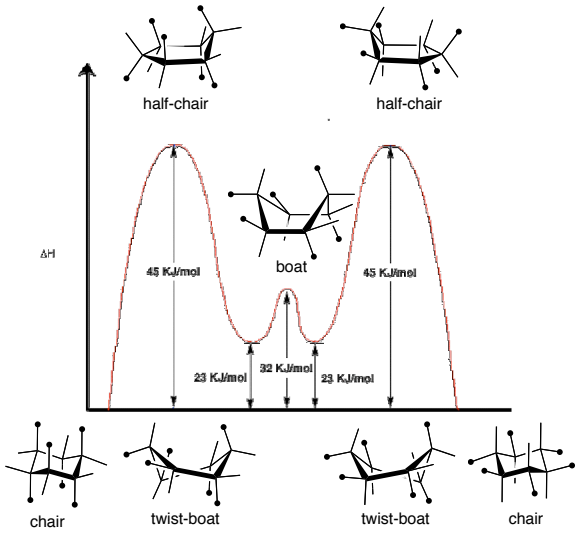
Ring flip interchanges the axial and equatorial positions

Chair-Chair Interconversion of Cyclohexane



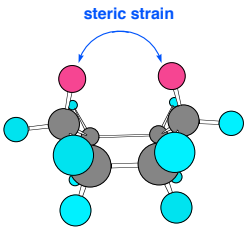
Energy Profile for the Chair-Chair Interconversion of Cyclohexane

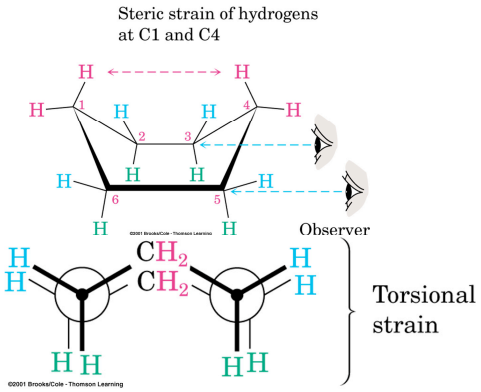
http://www2.chem.ucalgary.ca/Flash/cyclohexane.html



Boat cyclohexane (29 KJ/mol higher than chair)

no angle strain, considerable torsional strain, some steric strain

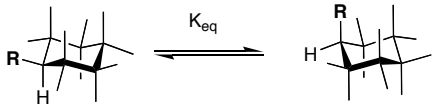


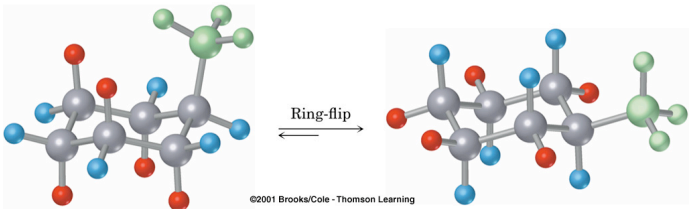


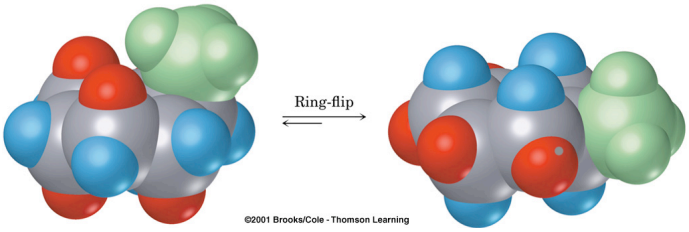
Twist-boat cyclohexane (23 KJ/mol higher than chair)

some torsional and steric strain relieved from the boat or half chair conformation.

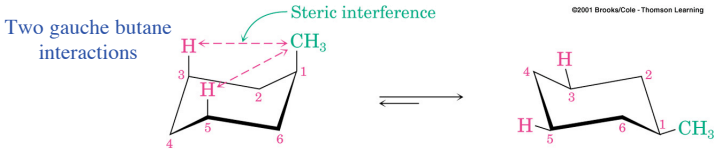
Conformation of Substituted Cyclohexanes

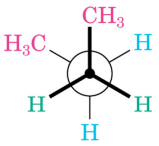




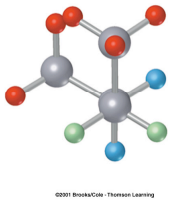


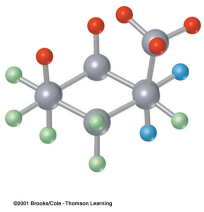
The axial position is more sterically hindered due to steric strain

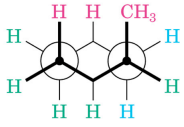




Gauche butane (3.8 kJ/mol strain)

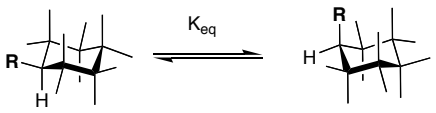






Axial methylcyclohexane (7.6 kJ/mol strain)

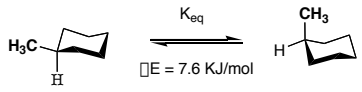
Two "gauche butane" interactions for axial methylcyclohexane
2 x 3.8 = 7.6 KJ/mol



Ring-clip exchanges the equatorial and axial positions of cyclohexane
an equatorial substituent become axial upon a ring-flip
Axial position is more sterically congested and is therefore less favored thermodynamically
The equilibrium constant is related to the energy difference by:

$\Delta E = -RT \ln K_{eq}$

for R=CH_3, ΔE is 7.6 KJ/mol
R= 8.3 x 10^{-3} KJ/mol, T= 300 °K (room temp)
K_{eq}= 0.048 95.4 % equatorial and 4.6 % axial at room temp



$7.6 = -(300\ °K)\ (8.3 \times 10\text{-}3\ KJ/\ mol)(\ln K_{eq})$

$-3.05 = \ln K_{eq}$

$K_{eq} = 0.048$

$$K_{eq} = \frac{[axial]}{[equatorial]}$$

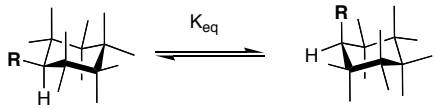
[axial] = x
[equatorial] = 1-x

$$K_{eq} = \frac{[\ x\ ]}{[1\text{-}x\ ]} = 0.048$$

$0.048 - 0.048x = x$

$.048 = 1.048x$

x= 0.954 = 95.4 % equatorial, 4.6 % axial

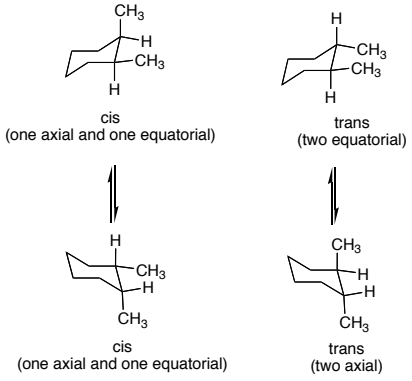


Substituent	per 1,3-diaxial interaction (KJ/mol)	total strain energy (A-value)	eq./axial
-F	0.5	1.0	60:40
-Cl	1.4	2.8	70:30
-Br	1.4	2.8	70:30
-I	0.85	1.7	65:34
-OH	2.1	4.2	85:15
$-NH_2$	2.7	5.4	90:10
$-N(CH_3)_2$	4.4	8.8	97:3
$-CH_3$	3.8	7.6	95:5
$-CH_2CH_3$	4.0	8.0	96:4
$-CH(CH_3)_2$	4.6	9.2	96:4
$-C(CH_3)_3$	> 8	16	>> 99.9:0.1
$-CH_2C(CH_3)_3$	4.2	8.4	97:3
$-C_6H_5$	6.3	12.6	99.5:0.5
CO_2H	2.9	5.8	92:8
-CN	0.4	0.8	60:40

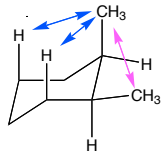
Disubstituted Cyclohexanes

relative stereochemistry: i.e, cis or trans

1,2-dimethylcyclohexane: two stereoisomers



For cis-1,2-dimethylcyclohexane



{2 x 3.8) + 3.8 = 11.4 KJ/mol

For trans-1,2-dimethylcyclohexane

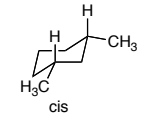
3.8 KJ/mol

□G= 11.4 KJ/mol

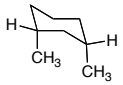
4 x 3.8 = 15.2 KJ/mol

K_{eq}= 0.01 (99 : 1)

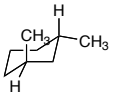
1,3-disubstituted



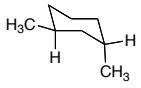
cis
(two equatorial)



cis
(two axial)

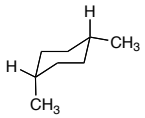


trans
(one equatorial, one axial)

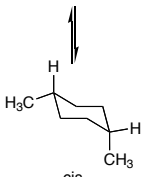


trans
(one equatorial, one axial)

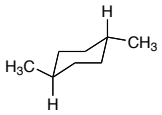
1,4-disubstituted



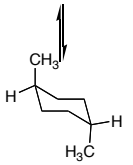
cis
(one equatorial, one axial)



cis
(one equatorial, one axial)

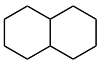


trans
(two equatorial)



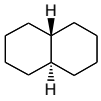
trans
(two axial)

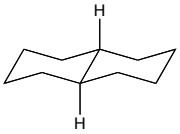
Polycyclic molecules

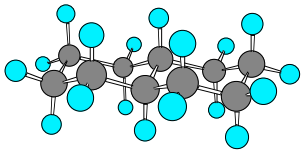


decalin: two fused cyclohexanes
two rings share two carbons, referred to as the bridgehead

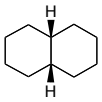
trans-decalin

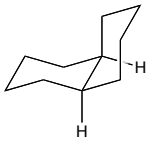


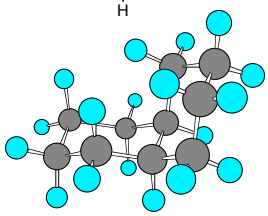




cis-decalin

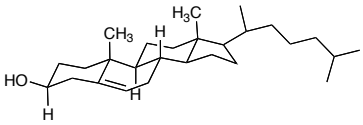


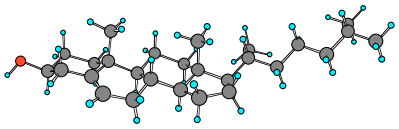


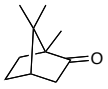


Cis- and trans-decalin are stereoisomers, they do not interconvert into each other

Cholesterol







Camphor

bridgehead carbons

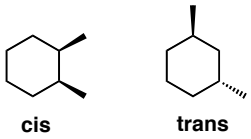
two 2-carbon bridges and one 1-carbon bridge

Bicyclo[2.2.1]heptane

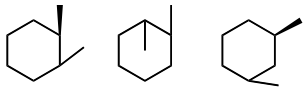
Drawing Structures

CYCLIC ALKANES: Substituents on a cyclic alkane can be either *cis* or *trans* to each other. You should draw the ring in the plane of the paper (solid lines) and use dashes and wedges to show whether substitutents are above or below the plane of the ring.

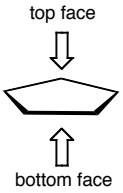
correct ☺

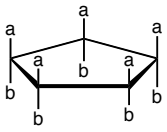


incorrect ☹

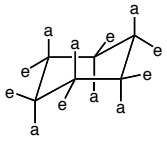


On occasion you may wish to distinguish the faces of a cycloalkane.



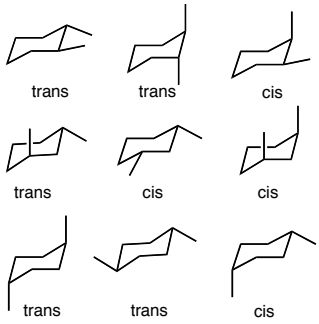


CYCLOHEXANE: For cyclohexanes you may be asked to draw a chair, in which case all substituents must be either axial or equatorial. The following is the correct way to draw chair cyclohexane. Note how the axial and equatorial substituents off each carbon are represented.



Disubstituted chair cyclohexanes:

correct ☺



incorrect ☹